I. C. 7481 OCTOBER 1948

UNITED STATES
DEPARTMENT OF THE INTERIOR
J. A. KRUG, SECRETARY

BUREAU OF MINES
JAMES BOYD, DIRECTOR

RECEIVED
NOV 8 - 1948
O. S. U. LIBRARY

INFORMATION CIRCULAR

METHODS OF PRODUCING ULTRA-CLEAN COAL FOR ELECTRODE CARBON IN GERMANY

BY

H. G. GRAHAM AND L. D. SCHMIDT

817565

Generated on 2024-09-19 19:39 GMT / https://hdl.handle.net/2027/osu.32435030643795
Public Domain, Google-digitized / http://www.hathitrust.org/access_use#pd-google
Digitized by Google
Original from THE OHIO STATE UNIVERSITY

I. C. 7481,
October 1948.

INFORMATION CIRCULAR

UNITED STATES DEPARTMENT OF THE INTERIOR - BUREAU OF MINES

METHODS OF PRODUCING ULTRA-CLEAN COAL FOR ELECTRODE CARBON IN GERMANY[1]

By H. G. Graham[2] and L. D. Schmidt[3]

CONTENTS

	Page
Summary	1
Description of Processes	3
Froth flotation without chemical treatment and electrostatic separation	3
Froth flotation followed by acid extraction	5
Coal-cleaning process	5
Chemical-extraction plant	6
The Ruhrwerks coal-cleaning process	7
Ash removal by jig-washing and caustic extraction	8
Coal-cleaning process - description of projected plant	8
Chemical-extraction process - description of projected plant	9
De-ashing of coal by forming a coal-oil paste	11
Pott-Broche process	12
Summary and conclusion	13

SUMMARY

Several processes for the production of ultra-clean coal for electrode carbon were developed in Germany prior to and during World War II. These processes have been investigated since the end of the war by the British and U. S. Government missions. As the reports of the investigations are not readily available to the public, it is the purpose of this paper to present the information which has been obtained regarding the methods by which ultra-clean coal was produced.

Almost all the ultra-clean coal was used in the manufacture of electrodes for the production of aluminum and magnesium. Standard raw materials for making these electrodes are pitch coke and petroleum coke, which are nearly

1/ Work completed on manuscript in April 1948. The Bureau of Mines will welcome reprinting of this paper, provided the following footnote acknowledgment is used: "Reprinted from Bureau of Mines Information Circular 7481."

2/ Mining engineer, Synthesis Gas Production Laboratories, U. S. Bureau of Mines, Morgantown, W. Va.

3/ Chief, Synthesis Gas Production Branch, U. S. Bureau of Mines, Morgantown, W. Va.

Generated on 2024-09-19 19:48 GMT / https://hdl.handle.net/2027/osu.32435030643795
Public Domain, Google-digitized / http://www.hathitrust.org/access_use#pd-google
Digitized by Google
Original from THE OHIO STATE UNIVERSITY

ashless. The inclusion of ash in the electrode carbon results in lowered efficiency and impure metal from the reduction process. Petroleum coke and pitch coke were in very short supply in Germany during the war, so that it was necessary to augment the supply with carbon produced from coal. In the emergency, methods were developed to clean coal which had never before been economically feasible. However, a demand for nearly ash-free coal might develop in the United States if a shortage of petroleum coke were to occur at the same time as a strong demand for light metals. Other uses of ultra-clean coal are in direct hydrogenation of coal, in production of activated carbon, and for special fuels.

Specifications for electrode carbon are rather severe owing to the necessity for producing pure metal. Maximum amounts of impurities allowable in American practice are as follows:

Total ash, 1.0 percent (in finished coke, 0.7 percent)
Silica, 0.08 percent Ca or Na, or their sum, 0.12 percent
Sulfur, 2.0 percent Ba, Ni, Cr, Mn, Co, and V are objectionable in very small amounts.

The most important process for ultra cleaning of coal in Germany was froth flotation. Froth flotation had been used widely there to process washery-water sludges and to recover coking coal from high-ash fines. Its use was indicated, therefore, when the demand for ultra low-ash coal arose. In two plants the coal cleaned by froth flotation was treated with acid or caustic to lower further the ash content. Another process used on an industrial scale was that of dissolving the coal substance in the middle oil from direct hydrogenation of coal under controlled pressure and temperature. The resulting paste was heated, filtered, and the oil distilled off. The residue was a low-ash organic material that could be carbonized for electrode carbon or could be hydrogenated directly. Several other processes had been developed to the laboratory or pilot-plant stage but had never been used on a commercial scale. These processes included cleaning by centrifugal action, cleaning by electrostatic action, and cleaning by forming a paste with oil in water.

The coal-preparation plants at the Carl Alexander mine, Augusta Viktoria mine, and Kőenigin Elisabeth mine are described in Bureau of Mines Information Circular 7389: "Coal Preparation Practice in Western Germany", by Thomas Fraser and M. G. Driessen. Most of the special equipment used at these plants is described in the above publication.

The ultra-clean coal required coking and calcination before it was ready for electrode manufacture.4/5/6/7/ Coking was carried out in conventional-type

4/ Rice, A. J., and Frary, Francis C., Carbon Electrodes in Germany for the Aluminum Reduction Industry: Office of the Military Government for Germany (U.S.), FIAT Final Report 986, 19 November 1946.

5/ Wikle, Hugh G., and Steiner, Walter A., Survey of the Carbon and Graphite Electrode Industry of Germany: Joint Intelligence Objectives Agency, FIAT Final Report No. 397, 17 November 1945.

6/ Perrycoste, W. B. C., German Carbon Electrode Manufacture at Griesheim (I.G.F.): H. M. Stationery Office, London, BIOS Final Report No. 338, Item Nos. 21, 22, 23, February 1946.

7/ Purdon, F. F., Carbon Electrodes I. G. Farben, Griesheim: H. M. Stationery Office, London, BIOS Final Report No. 258, Item No. 22.

Generated on 2024-09-19 19:43 GMT / https://hdl.handle.net/2027/osu.32435030643795
Public Domain, Google-digitized / http://www.hathitrust.org/access_use#pd-google
Digitized by Google
Original from THE OHIO STATE UNIVERSITY

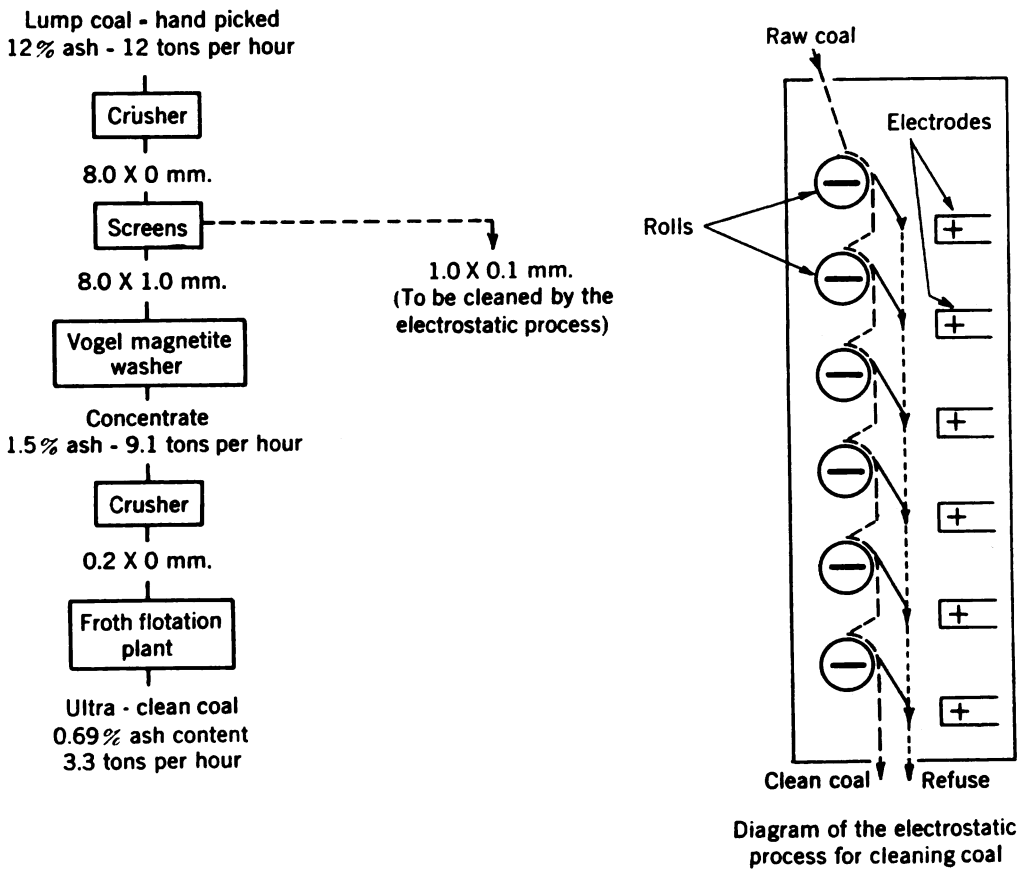

Figure 1. - Method of producing ultra-clean coal at the Königin Elizabeth Colliery; also, the electrostatic coal cleaning process.

Generated on 2024-09-19 19:50 GMT / https://hdl.handle.net/2027/osu.32435030643795
Public Domain, Google-digitized / http://www.hathitrust.org/access_use#pd-google
Digitized by Google
Original from THE OHIO STATE UNIVERSITY

byproduct ovens at high temperatures. Calcination was effected in continuous-feed, vertical shaft-type kilns. When the volatile content of the coke was 5 percent or more, no auxiliary fuel was required to operate the kilns. Coke of less than 5 percent volatile matter required producer gas for heating. The calcined carbon from the kilns was crushed, mixed with pitch, pressed or extended to form electrodes, and baked in resistance-type electric furnaces. The finished electrode must be strong, hard, and dense. The final operations in the manufacture of electrodes do not lie within the scope of this report.

DESCRIPTION OF PROCESSES

Froth Flotation Without Chemical Treatment and Electrostatic Separation8/ (Fig. 1)

At the Königin Elizabeth colliery, crushed hand-picked lump coal was cleaned in two stages to 0.5 percent ash content. The raw lump coal with ash content of 12 percent was hand-picked, crushed to pass an 8.0 mm. screen (approx. 5/16 inch), dedusted at 0.1 mm. (approx. #140 U. S. sieve series), and rescreened at 1.0 mm. (No. 180 sieve), and the 8.0 x 1.0 mm. size was washed in a "Streamline" washer designed by Dr. Vogel, which used magnetite in suspension to form a heavy medium for specific-gravity separation. The following data are given as typical of the performance of this washer:

	Yield, percent	Ash, percent	Sp. gr. float coal
Clean coal	76	1.5	1.35
Middlings	8	12.0	1.90
Dirt	10	65.0	1.90

This leaves 6 percent of the coal containing approximately 57 percent ash unaccounted for. Both the composition of the coal and the performance of the washer must have been exceptional to obtain a yield of 76 percent of 1.5 percent ash content. The washed coal was rinsed with water to remove the magnetite, which was recovered from the water by magnetic action. The cleaned coal was again crushed to pass 0.2 mm. screen (approx. No. 70 sieve), and was recleaned in conventional flotation machines. The flotation plant consisted of 15 double cells of 4,200 litres capacity each (approx. 1,105 gal.) arranged in three banks of five. Apparently the froth was recleaned four times. The final concentrate had an ash content of 0.5 to 0.7 percent and represented 26.8 percent of the raw coal. The concentrate was dewatered by centrifugal action. The three centrifugal machines were made by Escher Wyss Maschinenfabrik of Ravensburg. They were automatically operated in intermittent stages allowing the coal to build up on the inner wall of a cylindrical rotor. The capacity of each machine was about 4 tons per hour, and the moisture content of the output coal was 22.5 percent. The coal was mixed with half its weight of pitch and was coked. Following is a summary of the cleaning process:

8/ Wilkins, E. T., The Preparation of Ultra-Clean Coal at the Königin Elizabeth Colliery, Essen-Frillendorf (Mannesmannröhren Werke A. G.), Combined Intelligence Objectives Sub-Committee Report, Item No. 30, File XXXIII-6: H. M. Stationery Office, London, England.

Generated on 2024-09-19 19:47 GMT / https://hdl.handle.net/2027/osu.32435030643795
Public Domain, Google-digitized / http://www.hathitrust.org/access_use#pd-google
Digitized by Google
Original from THE OHIO STATE UNIVERSITY

Products	Analysis, percent		Output, metric	
	Ash	Moisture	Tons/hr.	Percent
Raw coal	12.0	2	12.1	100.0
Lump refuse (Hand-picked)	-	-	0.3	2.3
Fine dust (0.1 mm.)	7.0	1	0.7	5.5
Coarse dust (1.0-0.1)	6.0	1	3.5	29.5
Vogel refuse (sp.gr. 1.9)	69.0	16	1.2	10.1
Vogel middlings (sp.gr. 1.35-1.9)	12.0-26.0	12	0.6	5.0
Froth flotation tailings	4.2	22.6	2.5	20.8
Froth flotation clean coal	0.69	22.5	3.3	26.8

It is not stated why no attempt was made to process the dust from the initial crushing of the lump coal by froth flotation. It may have been necessary to make the specific-gravity separation at 1.35 specific gravity before attempting to produce ultra-clean coal by flotation. An electrostatic dry-cleaning plant had been installed but not operated at this mine for preliminary treatment of the 1.0 by 0.1 mm. dust referred to above, which comprised 29.5 percent of the raw coal. The plant was made up of six tall, boxlike units designed to handle 2 tons per hour each. The separation was to be accomplished by feeding coal over an electrically charged roll and allowing it to fall past an electrode. The potential between the roll and the electrode was 30,000 to 50,000 volts. Particles of high ash content were deflected towards the electrode, whereas the coal particles fell vertically. Each unit contained six sets of rolls and electrodes, over which the coal passed in succession. As the plant had not been operated, its performance was not known. Data obtained at a pilot plant had indicated that a coal of 8 to 10 percent ash content would be cleaned to 1.5 to 4.0 percent ash. The coal cleaned electrostatically was to have been processed further by froth flotation in the same manner as that from the Vogel washer.

The cleaning of fine coal by electrostatic methods was thoroughly investigated prior to the development of this separator.2/ The process is applicable to coals of medium-volatile and anthracitic rank. It presents special advantages in the recovery of strongly-coking constituents of friable coals. Other advantages are low power consumption and avoidance of difficulties connected with handling wet coal.

2/ Crawford, A., Metallgesellschaft A. G. and Lurgi Bau, Frankfurt Am Main. Electrostatic Separation of Coal and Other Minerals: H. M. Stationery Office, London, B.I.O.S. Final Report No. 1035, Item No's 21 and 30.

Generated on 2024-09-19 19:49 GMT / https://hdl.handle.net/2027/osu.32435030643795
Public Domain, Google-digitized / http://www.hathitrust.org/access_use#pd-google
Digitized by Google
Original from THE OHIO STATE UNIVERSITY

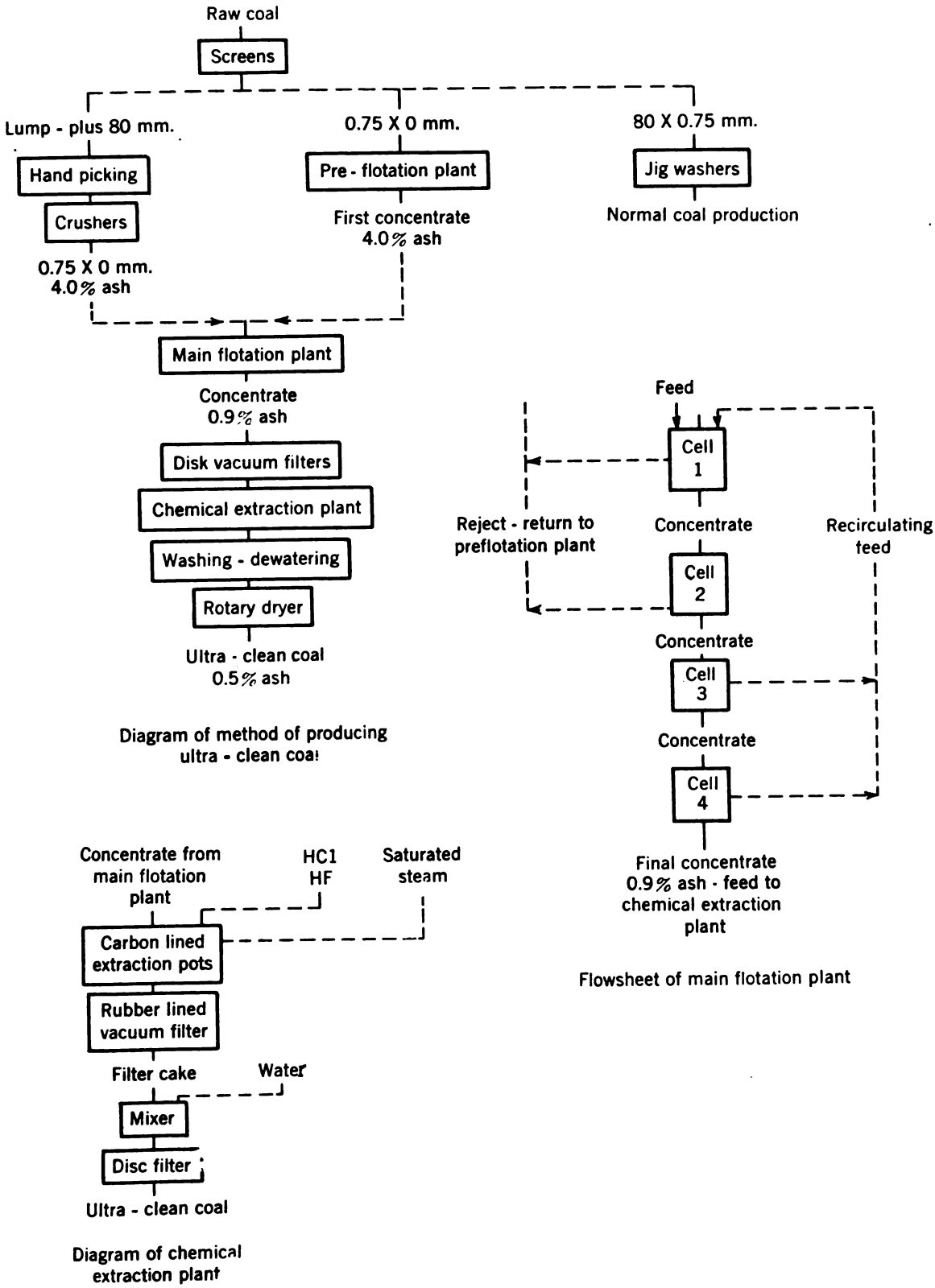

Figure 2. - Method of producing ultra-clean coal at Carl Alexander mine, Baesweiler.

Generated on 2024-09-19 19:44 GMT / https://hdl.handle.net/2027/osu.32435030643795
Public Domain, Google-digitized / http://www.hathitrust.org/access_use#pd-google
Digitized by Google
Original from THE OHIO STATE UNIVERSITY

Froth Flotation Followed by Acid Extraction[10/11/]

Six thousand tons of ultra-clean coal per month were produced at Baesweiler by froth flotation followed by acid extraction of ash. The feed to the main of final flotation cells was froth-skimmed from the initial stages of primary flotation of fines screened from the raw coal; plus crushed, hand-picked lump from a low-ash bed. It was desired to keep the quantity of lump fed to the flotation plant to a minimum, as it was the product of highest value produced at the plant. The rather complicated cleaning circuit was so arranged that discard from the main flotation cells was recleaned in the primary cells and probably appeared as ordinary clean coal used for byproduct coke making. The acid extraction process was a batch operation in which the coal was mixed with dilute hydrochloric and hydrofluoric acids at 100° C. for 1 hour.

Subsequently, the coal-acid mixture was filtered to remove the acid and twice stirred with water and refiltered. Processed coal, partly heat-dried, was coked in byproduct ovens to provide carbon of 0.65 percent ash content for electrode manufacture.

Coal-Cleaning Process

The raw coal was screened into several size ranges, of which the plus 80 mm. (about 3-1/4-inch) lump and the 0.75 x 0 mm. (minus No. 25 sieve) produced the feed for the final flotation plant. The intermediate sizes were jig-washed and charged to byproduct ovens. Lump coal from seam D, which averaged 4 percent ash when hand-picked, was kept separate, and enough was crushed and added to the main flotation plant to keep it operating at capacity. The greater source of ultra-clean coal was the 0.75 x 0 mm. fines. Ordinarily this coal would have been cleaned by froth flotation to make coking coal. For ultra-clean coal the froth was taken from the first three of 19 cells in the primary flotation plant. Data on this plant are as follows:

	Tons/hr.	Percent ash content
Feed	-	20-25
Concentrate	21	4
Middlings (coking coal)	37	6.7
Reject	24	70.0

10/ Schmidt, L. D., Production of Low-Ash Coke at the Carl Alexander Gewerkschaft, Baesweiler, Germany: Combined Intelligence Objectives Sub-Committee Report.

11/ Crawford, A., Carl Alexander Mine, Baesweiler near Alsdorf--The De-ashing of Coal by Froth Flotation and Acid Extraction, and the Ruhrwerks Coal Cleaning Process: British Intelligence Objectives Sub-Committee Final Report No. 523, Item No. 30, H. M. Stationery Office, London, England.

Generated on 2024-09-19 19:40 GMT / https://hdl.handle.net/2027/osu.32435030643795
Public Domain, Google-digitized / http://www.hathitrust.org/access_use#pd-google
Digitized by Google
Original from THE OHIO STATE UNIVERSITY

The flotation agent used was beechwood tar oil. Apparently in this plant the coal-water suspension passed through all the cells in turn and there was no recleaning of the froth. The skimmed froth was sent to the main flotation plant, which also received about 5 tons per hour of the hand-picked lump crushed to slightly larger than 0.75 mm. The main flotation plant contained 96 cells in groups of four, plus 20 standby cells. The froth was successively recleaned three times. Discard in suspension from the first two cells was returned via a 0.75 mm. screen to the primary flotation unit. The plus 0.75 mm. particles (from the crushing of lump coal) were ground wet in a ball mill and returned to the main flotation plant. Discard in suspension from the last two cells in each unit was again recirculated through the first two cells. As only the discarded suspension from the first two cells and the froth from the last cell were removed from the circuit, the intermediate particles must have recirculated five or ten times before finally being accepted or rejected. This fact accounts for the large cell capacity necessary to clean a relatively small tonnage of coal. Twelve tons per hour of coal at 0.9 percent ash content were produced. The coal was dewatered on rotary disk filters before going to the chemical-extraction process.

Chemical-Extraction Plant

The chemical-extraction process operated under German Patent No. D.R.P.B. 185,549 VI b/Ia. It was a batch process carried out in 10 of 13 pots. Each pot measured 3 meters (approx. 10 ft.) in diameter and 6 meters (20 ft.) in height. The bottom was an inverted cone with a plug hole in the center. The outer shells of the pots were reinforced concrete. They were lined on the inside with carbon blocks closely fitted and cemented with pitch. The blocks were made from coal produced at this mine, which had been mixed with pitch and carbonized at 1,500° to 2,000° C. Roofs and steam entrance pipes also were made of this material. The coal was mixed with twice its weight of acid solution and heated for 1 hour at 100° C. Heat was supplied by blowing in live steam, which probably also served to agitate the mix. The acid solution was given as 5 percent of commercial-strength hydrochloric and hydrofluoric acids in equal parts plus 95 percent water. Apparently this concentration produced the optimum ash removal per amount of acid used. Most of the acid was consumed in the process. The coal was freed of acid by filtering in rubber-lined disk filters, which were fitted with cloth of a synthetic acid-proof material called "Spalatite." After filtering, the coal was mixed with water and again filtered. At this stage, disk filters equipped with phosphor-bronze wire cloth were used. The dewatered coal still contained about 25 percent moisture, so that a portion of it had to be heat-dried in a horizontal rotary retort in order to bring the over-all moisture content down to 18 percent. At this point the ash content of the coal on the dry basis was 0.5 percent. The main advantage of the acid-extraction process is that a much greater yield of ultra-clean coal can be obtained than by using purely mechanical cleaning processes.

The coal was coked in conventional byproduct ovens of the Otto underjet design. The ovens were constructed of silica brick (rare in European practice) and were operated at a maximum temperature of 1,300° C. (2,372° F.).

Generated on 2024-09-19 19:43 GMT / https://hdl.handle.net/2027/osu.32435030643795
Public Domain, Google-digitized / http://www.hathitrust.org/access_use#pd-google
Digitized by Google
Original from THE OHIO STATE UNIVERSITY

This temperature was necessary to produce coke of less than 0.5 percent volatile matter and high electrical conductivity. The coke was carefully hand-quenched to limit the moisture to less than 0.5 percent. It was claimed that the coke produced from the chemically treated coal was as strong as that from untreated coal. The silica brickwork of the oven showed no corrosive effect from the acid used. An average analysis of the ash from the electrode coke over a period of 1 month was as follows:

	Percent
Total ash content	0.6 or 0.7
Silica (SiO_2)	46.12
Ferric oxide (Fe_2O_3)	15.32
Alumina (Al_2O_3)	23.65
Lime (CaO)	3.92
Magnesia (MgO)	0.50
Titania (TiO_2)	3.90
Sulfate (not determined)	-
Alkalies (not determined)	-
	93.41

The price of the electrode coke was fixed at 90 marks per ton. This was about three times the price of ordinary coke.

The process, as outlined above, was designed to produce the greatest possible amount of ultra-clean coal of a purity sufficient for the coke to meet the specifications for electrode carbon. Possibly it would have been cheaper to process more coal by froth flotation to obtain the desired amount if it proved possible to clean coal to the requisite ash content. The flotation flowsheet seems to be unnecessarily complicated. No data are available on comparable processes, but it appears possible that the cost of flotation at this plant could have been reduced at some sacrifice of cleaning efficiency.

The Ruhrwerks Coal-Cleaning Process[12/]

In view of the fact that chemical processes are expensive, the so-called "wet mechanical process" was developed. In this process the separation depends on centrifugal force and is used where other mechanical processes are insufficient.

Two commercial-size plants using this process have been erected in Germany - one for cleaning coal to 0.2 percent ash content at the Grube Donnersmark at Beuthen, and the other for recovering arsenical pyrites.

The process is carried out in a cylindrical vertical cell fitted with four fixed baffles and has a stirrer or propeller arranged at its lower end. A set of annular rings of semicircular cross section can be submerged in the liquid in the cell or withdrawn from it. The rings and stirrer rotate at sufficiently high speed to bring centrifugal force into action. With the rings submerged, the heavy particles are trapped on their inner sides and, by withdrawal of the rings, are removed from the liquid. Any heavy particles

12/ Crawford, A., Work cited in footnote 9.

Generated on 2024-09-19 19:45 GMT / https://hdl.handle.net/2027/osu.32435030643795
Public Domain, Google-digitized / http://www.hathitrust.org/access_use#pd-google
Digitized by Google
Original from THE OHIO STATE UNIVERSITY

not trapped by the rings collect on the side of the cylinder and are flung back to the center by the baffles. When the rings are in the raised position, the heavy particles are removed by a jet of water. The rings are raised and lowered periodically, the time of submersion being 30 seconds. A continuous flow is maintained through the cells, which may be connected in series or parallel, as in the case of froth-flotation practice.

Ash Removal by Jig-Washing Froth Flotation and Caustic Extraction[13/]

One hundred and twenty kg. of coke per day was produced by this method at the Auguste Viktoria mine, Huls, Recklinghausen. Equipment to produce 28 tons per hour had been constructed but had not been delivered to the mine. The process, therefore, had never been operated except on a laboratory scale.

Coal-Cleaning Process - Description of Projected Plant

The Auguste Viktoria mine produced coking coal with 12 percent ash in the raw coal and 22 percent volatile matter on the ash- and moisture-free basis. An existing jig washer produced 126 tons per hour of washed fines size 12.5 x 0 mm. (approx. minus 1/2 inch). The ash content of the fines was 8 percent. These fines were the raw material for the ultra-clean coal-recovery plant. The very fine particles were removed by an 0.5 mm. screen (No. 35 sieve) and were sent to the coke ovens. This operation reduced the ash content of the 12.5 x 0.5 mm. size to 4.0 percent, as the screenings contained 12 percent ash. The coal was then to be washed a second time in nine creaming jigs and was to be separated into four fractions, as shown in the table below:

Fraction	Tons/hr.	Percent ash content
Very clean coal	28	1.8
Coking coal	24.6	4.0
Middlings	5.7	18.0
Slurry	4.7	-

After the creaming jig, the clean coal was dewatered centrifugally. There were two centrifuges, each with a capacity of 40 tons per hour, one acting as a standby unit. Before froth flotation, the dewatered coal was crushed in two coarse crushers (type not mentioned) and six "Teutonia" disk mills of 5 tons per hour capacity each. The sizing of the crushed coal was as follows:

13/ Crawford, A., I. G. Farbenindustrie A. G. Höchst - The De-ashing of Coal by Combined Jig Washing, Froth Flotation, and Extraction with Caustic Soda: British Intelligence Objectives Sub-Committee Final Report No. 522, Item No. 30, H. M. Stationery Office, London, England.

Generated on 2024-09-19 19:41 GMT / https://hdl.handle.net/2027/osu.32435030643795
Public Domain, Google-digitized / http://www.hathitrust.org/access_use#pd-google
Digitized by Google
Original from THE OHIO STATE UNIVERSITY

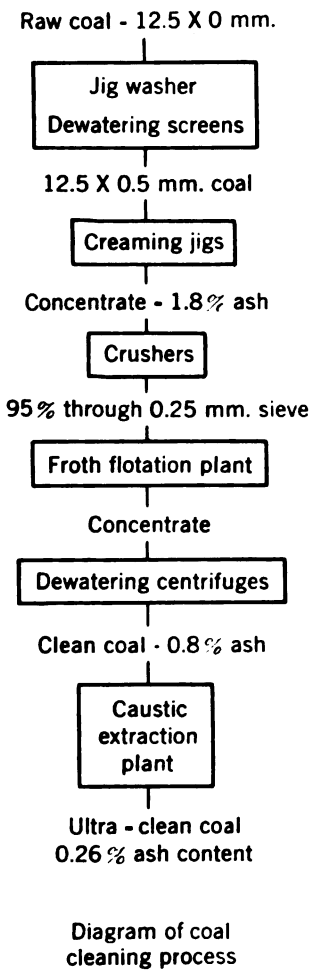

Diagram of coal cleaning process

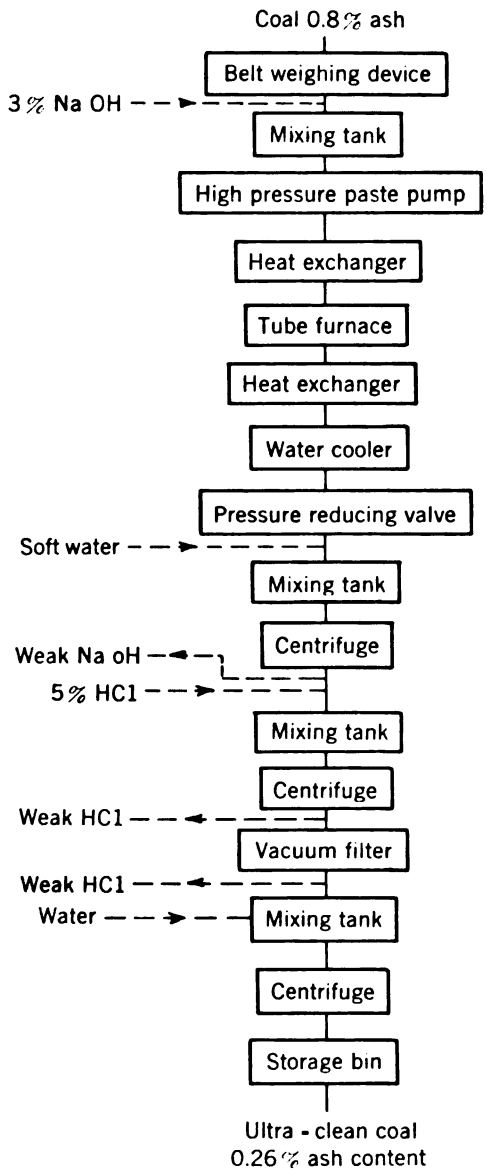

Diagram of caustic extraction process

Figure 3. - Method of producing ultra-clean coal at the Auguste Viktoria mine, Hüls, Recklinghausen.

Generated on 2024-09-19 19:41 GMT / https://hdl.handle.net/2027/osu.32435030643795
Public Domain, Google-digitized / http://www.hathitrust.org/access_use#pd-google
Digitized by Google
Original from THE OHIO STATE UNIVERSITY

Through	On	Percent
-	0.52 mm.	1
0.52 mm.	0.25 mm.	5
0.25 mm.	0.12 mm.	16
0.12 mm.	0.09 mm.	10
0.09 mm.	0.06 mm.	17
0.06 mm.	-	51

The coal was ground, therefore, to about 50 percent through 200 mesh.

The froth flotation cells were arranged in three banks, 14 cells in the first and 10 cells in each of the other two. Each bank of cells included a conditioner preceding and a froth breaker succeeding the unit. This equipment was not described. The coal was to be floated in the first unit and the froth broken up and refloated twice. A yield of 55 percent or 15.4 tons per hour, of coal with 0.8 percent ash content was expected. This was to be dewatered in two Escher-Wyss centrifuges to a moisture content of 10 percent. It was claimed that the froth flotation cleaning removed iron compounds, which, if allowed to be present, would interfere with the chemical-extraction stage.

Chemical-Extraction Process - Description of Projected Plant

The caustic soda extraction plant was designed to treat the caustic soda paste at 250° C. and 100 to 200 atmosphere pressure for 20 minutes and then wash out the caustic. The caustic was added to the coal in one of three tanks fitted with stirrers. Forty percent of the weight of the coal was the amount of caustic used; its concentration was 3.0 percent. With the 10 percent of water in the coal, the caustic concentration became 2.5 percent. The mixture was stirred for 30 minutes at atmospheric pressure and 40° to 50° C. It was then pumped into the tube-heating furnace through a heat exchanger in which the hot outgoing mixture preheated that entering the furnace. Three high-pressure paste pumps were used for conveying the mix. The paste was retained at 100 to 200 atmospheres pressure in the tube-heating furnace and was heated to 250° C. The paste remained in the furnace for 20 minutes. Leaving the furnace through the heat exchanger, the paste was cooled by water and passed through pressure-reducing valves to a collecting pot. The six pots were used for temporary storage preceding the dewatering centrifuges. These were five rubber-lined centrifuges, which, in conjunction with the collecting pots and various pumps, were employed for the following operations:

1. The caustic soda solution was centrifuged off and returned to use.
2. The coal was dropped into a 5 percent solution of HCl and stirred.
3. The HCl solution was centrifuged off for reuse.
4. The coal was dropped into soft water and stirred.
5. The coal was partly dewatered by centrifuging and further dewatered by filtering in rubber-lined vacuum filters that employed cloth made from poly-vinyl chloride.

The diluted caustic soda was employed for water softening. Excess caustic was neutralized with dilute HCl washings and was wasted. Twenty-one kg. of caustic soda and 63 kg. of 30 percent HCl were consumed per ton of coal treated.

Generated on 2024-09-19 19:39 GMT / https://hdl.handle.net/2027/osu.32435030643795
Public Domain, Google-digitized / http://www.hathitrust.org/access_use#pd-google
Digitized by Google
Original from THE OHIO STATE UNIVERSITY

After the filter treatment, the coal was again mixed with water, stirred, and centrifuged. The final product was coal containing 10 percent moisture and 0.28 percent ash.

The coking strength of a good coking coal was about half destroyed by the process. The Auguste Viktoria coal, however, retained some coking properties after 2 days' extraction. Three days' extraction produced a noncaking residue. Analysis of the ash is given as follows:

Stage	Raw Coal		Flotation product		Extracted coal	
Ash, percent	4.7		0.76		0.26	
Constituent	Percent ash	Percent coal	Percent ash	Percent coal	Percent ash	Percent coal
SiO_2	42.52	2.04	28.96	0.22	24.26	0.063
Fe_2O_3	12.38	.58	29.38	.22	38.72	.101
Al_2O_3	32.72	1.54	34.19	.26	27.51	.072
CaO	3.36	.15	2.18	.016	1.79	.005
MgO	1.31	.06	1.59	.012	1.04	.003
SO_3	2.63	.12	1.09	.008	.56	.0015
Alkali	3.41	.76	2.21	.017	5.32	.014
TiO_2	-	-	.40	.003	.50	.0013

The experimental coke oven had been built to carbonize the 120 kg. of coal per day produced by this process. The oven was gas-fired at a flue temperature of 1,300° C, and coked at an effective temperature of 1,100° C. Twenty tons of coke was made in this oven for full-scale electrode trials.

After the ash content of the coke, its most important quality was its electrical resistance. In order to test this, a sample was ground and screened between 0.06 and 0.09 mm. The closely sized sample was placed in a steel cylinder of 30 mm. inside diameter, which was equipped with insulated electrodes 25 mm. apart. The cell was filled under standard conditions (probably care was taken that no large voids existed), and a small hydraulic piston put a pressure of 5 atmospheres on the charge. The resistance of the sample between the electrodes then was determined. Good coke was said to have a resistance of 300 ohms under these conditions.

The cost of a plant to produce coke by this process is estimated at 7,835,000 Rm. on a basis of 50,000 tons per year. The cost of materials, services, and labor under these conditions was estimated at 39.54 Rm. per ton. The cost of ultra-clean coal before coking was expected to be 108 Rm. per ton. This is in contrast to a cost of raw coal probably below 10 Rm. per ton.

This process appears to have been extremely complicated compared to most processes for treating coal. For example, the coal was dewatered centrifugally six times during treatment and was vacuum-filtered once. The centrifuges following the extraction stage were rubber-lined, and the piping, tanks, pumps, etc., must have been made of special alloy to resist corrosion.

Generated on 2024-09-19 19:49 GMT / https://hdl.handle.net/2027/osu.32435030643795
Public Domain, Google-digitized / http://www.hathitrust.org/access_use#pd-google
Digitized by Google
Original from THE OHIO STATE UNIVERSITY

The tube-heating furnace would have been difficult to construct and expensive to operate. Over all, the process would only be possible at a greatly increased price for the coal produced, probably seven or eight times the cost of ordinary clean coal.

De-ashing of Coal by Forming a Coal-Oil Paste[14/]

This method was developed to process lignite for direct hydrogenation. It was found that by kneading the middle or sump oil from the hydrogenation process with the finely ground coal suspended in water, a coal-oil paste was formed that left the high-ash particles in the water. The process was made commercially feasible by the development of kneading pumps to mix the materials and to separate the water. Certain coals required acid treatment in order to be cleaned by this method. The paste of oil and clean coal may be used for direct hydrogenation or for the manufacture of carbon electrodes. When coked to make electrodes, more than enough oil is recovered to carry on the process.

The lignite used for hydrogenation at Leuna had an ash content of 13 percent and moisture content of 50 percent. For hydrogenation, the lignite was first heat-dried, then ground with lubricating oil from the hydrogenation process to make a paste. After adding catalyst, it was passed into the hydrogenation chamber. The ash and catalyst were recovered after hydrogenation in a slimy sediment, which contained about 65 percent organic material. The initial heat-drying of the lignite and the processing of the sediment were very expensive factors in the hydrogenation process. Experiments with raw Leuna lignite mixed with 55 kg. of oil per metric ton of coal reduced the ash content from 13 to 3 percent. At the same time, about two-thirds of the moisture content of the coal was removed, thus cutting down the expense of drying the coal. It was necessary to use HCl with the coal in order to achieve efficient separation. Another experiment at Höchst also used acid for treating the coal. The acid was added to the coal in a premixing worm, and the oil was added in a second mixing worm. The mixture was discharged from the second worm just as the "change of phase" occurred. The "change of phase" is the point where the coal and oil separate from the water. The mixture then entered the first of four kneading pumps, which "work" the mixture much as butter may be worked to expel milk and water. The kneading pumps were long spiral pumps, containing two interlocking spirals cut in such a way that their capacity at the discharge end was one-third that of the intake end. During its movement through the pumps, the paste was continually squeezed back through the clearance around the spirals, thus producing the kneading action. Rinsing water was added before the mixture entered the pumps. Ash reduction to 3 percent was accomplished with one pass through the system, whereas two passes produced an ash content of 2 percent.

It was found that by using the slime from the hydrogenation process directly instead of the oil separated from it, the ash constituents of the

14/ Winnacher, K., Entaschung von Braunkohle u. Steinkole für die Hydrurung und für aschearme Schwelproducte: Frankfurt a.M. - Hochst, February 1939.

Generated on 2024-09-19 19:44 GMT / https://hdl.handle.net/2027/osu.32435030643795
Public Domain, Google-digitized / http://www.hathitrust.org/access_use#pd-google
Digitized by Google
Original from THE OHIO STATE UNIVERSITY

slime were also removed in the cleaning process. By so doing, the expense of processing the slime was avoided, and the paste entering the hydrogenation chamber contained only 3 percent ash, in contrast to the 6 percent in normal operation.

The paste produced by this cleaning process could be coked at low temperatures to form a strong, dense coke. A special two-stage oven was designed and erected for this purpose. The first stage was a horizontal kiln through which briquettes of the paste were carried on a conveyor. The temperature was maintained at 400° C., which drove off most of the oil and hardened the briquettes. The second stage was a cylindrical, vertical, continuous oven operated at 720° C. The coke produced had volatile matter content of approximately 5 percent. Barely enough gas was produced to heat the oven, and 107 percent of the amount of oil required for the original processing was recovered.

Some thought was given to use of the process to produce coke for calcium carbide and carbon disulfide manufacture and for utilizing "salt coals" of the Leuna basin.

The process was operated at a rate of 500 kg. of coke produced per day. A pilot plant was to be erected to study costs and procedures more closely. As described, the process was slow, complicated, and expensive. The only way by which the oil may be recovered is by heat distillation. It is probable that coal containing medium-high ash particles could not be cleaned efficiently by this method. The cost of the product precludes its use for any but specialized purposes, such as direct hydrogenation.

The Pott-Broche Process[15/]

This process is reported in detail in Bureau of Mines Information Circular 7420, by H. H. Lowry and H. J. Rose, and will therefore only be summarized briefly here.

The process was developed to produce a liquid-phase material suitable for direct hydrogenation to oil and gasoline; however, it was actually used to produce electrode carbon of low ash content. The process consists of making a coal and oil paste, using sump oil from previous hydrogenation of coal. The paste is heated under high pressure which causes certain chemical changes to take place in the coal structure, which allow it to be dissolved in the oil. The oil and dissolved coal are filtered off, leaving most of the ash content in the filter cake. The coal is recovered by distilling off the oil. Coal is not, strictly speaking, the material produced. It is rather a solid hydrocarbon having some of the properties of coal. It is suitable for making electrode carbon or activated carbon or for direct hydrogenation.

15/ Lowry, H. H., and Rose, H. J., Pott-Broche Coal-Extraction Process and Plant of Ruhröl G. H., Bottrop-Welheim, Germany: Bureau of Mines Information Circular 7420, 1947, 12 pp.

Generated on 2024-09-19 19:39 GMT / https://hdl.handle.net/2027/osu.32435030643795
Public Domain, Google-digitized / http://www.hathitrust.org/access_use#pd-google
Digitized by Google
Original from THE OHIO STATE UNIVERSITY

The process depends on the use of the sump oil from hydrogenation, as the high hydrogen content of the oil is necessary for the depolymerization of the coal to soluble substances. The process is necessarily expensive and probably applicable only to special operations.

This process is somewhat similar to others that have been patented involving some oxidation of the coal with subsequent solution, filtration, and distillation. As far as is known, none have been applied commercially.

SUMMARY AND CONCLUSION

Raw coal, as it comes from the mine, consists of several materials of varying ash content. These may be classified as high-ash refuse, intermediate ash refuse, or middlings, and coal components of ash content ranging from intermediate to low. In order to produce ultra-clean coal, the general procedure was as follows:

1. Selection of a coal that contained an appreciable amount of low-ash material, the limiting value being 0.8 to 1.0 percent ash content. This coal must also contain little pyrite or such pyrites as may easily be removed during the primary cleaning.

2. Primary cleaning by hand-picking, jigging, or other cleaning method to eliminate pyrite and high-ash material.

3. Fine crushing in order to separate low-ash particles from others. This was necessary to produce the greatest possible amount of ultra-clean coal.

4. Cleaning of the crushed coal by froth flotation. It is emphasized that the German plants, which actually produced ultra-clean coal, used froth flotation as the final physical separation process. Separation was accomplished through several stages, involving recleaning of the products of the primary cells in dilute suspension in secondary cells and, in several instances, recirculation of middlings in order to achieve high separation efficiency.

5. In two instances, chemical treatment was used to further reduce the ash content of coal that had been cleaned nearly to the limit of low-ash content by physical means. The means employed were leaching with acid in one instance and leaching with caustic soda in the other. The effectiveness of this treatment, of course, was a function of the chemical properties of the coal being treated. Its use was an indication of the desperate need of low-ash coal in Germany, as chemical treatment greatly increased the cost of an already expensive product.

6. Drying of the product. Both chemically treated and froth-flotation coal required dewatering and drying before utilization. In most instances, dewatering was also required during the intermediate stages of preparation. The means employed for dewatering were screens, drainage bunkers, or centrifuges. Final drying to usable moisture content was done by noncontinuous centrifuges, continuous filters, or rotary heat dryers.

Generated on 2024-09-19 19:42 GMT / https://hdl.handle.net/2027/osu.32435030643795
Public Domain, Google-digitized / http://www.hathitrust.org/access_use#pd-google
Digitized by Google
Original from THE OHIO STATE UNIVERSITY